

The Application of Low-Resolution Microwave Spectroscopy to Conformational Analysis

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Abstract: The potential of low-resolution microwave spectroscopy of relatively large near symmetric top molecules for conformational analysis is developed. The theoretical origins, characteristics, and information content of the spectra are discussed. The usefulness of the technique is shown by a conformational analysis of cinnamaldehyde, *p*-anisaldehyde, and several ionones. The stereochemistry of cinnamaldehyde is established to be *s*-trans. The less stable *s*-cis conformer is also observed. *p*-Anisaldehyde is shown to be a mixture of planar and nonplanar rotomers. The axial-equatorial conformations and ring orientations of several ionones are established. The *cis*-*trans* stereochemistry of α -irone is also clarified.

High-resolution gas-phase rotational microwave spectroscopy is a powerful tool for conformational analysis,¹ since on the microwave time scale each vibrational state and conformation of the molecule is a distinct species. The technique is a very sensitive probe into molecular structure because of the high resolution possible. The molecular parameters obtained from a spectral assignment, the rotational constants, are directly related to molecular geometry. Except for work on symmetric tops, high-resolution studies have for the most part been limited to small molecules due to the difficulty of assigning the complex asymmetric rotor spectrum. Large molecules have small rotational constants and low-frequency vibrational modes. Consequently, at room temperature a large number of rotational-vibrational states are populated so that the intensity of an individual rotational transition is very weak. With the advent of rapidly scanning broad-banded spectrometers, Scharpen^{2a-c} discovered that moderately sized molecules (*ca.* 18-40 atoms) close to cylindrical symmetry often have a medium to strong, easily analyzed symmetric top band spectrum (*cf.* Figure 1). The strength of the bands results from the near superposition of many transitions, which is possible in a molecule close to the symmetric top limit. The bands are broad (*ca.* 50-200 MHz wide) so this spectroscopy will be referred to as low-resolution microwave spectroscopy (LRMW).

This paper treats the characteristics of an extraction of conformational information from such band spectra. Scharpen^{2a-c} has earlier used LRMW as a conformational tool. In the present study, the technique was applied to *trans*-cinnamaldehyde, *p*-anisaldehyde (III), and a series of ionones (Figure 2). *trans*-Cinnamaldehyde was found to exhibit two rotomers, *s*-*cis* and the more stable *s*-*trans*. The spectrum of III was assigned to two planar rotomers and one or more nonplanar rotomers. The axial-equatorial conformers and ring orientations of several ionones were established for the first time. LRMW also provided an independent determination of the stereochemistry of the isomeric

ionones, confirming the work of Ohloff and Rautenstrauch.^{2d}

Characteristics of LRMW Spectra

Theory of LRMW. A molecule is a symmetric top whenever two of the principal moments of inertia are equal. Only the prolate limit (cylindrical symmetry, $I_a < I_b = I_c$), the most common case, will be discussed here, but the general results hold equally well for the oblate limit ($I_a = I_b < I_c$). In the prolate limit, the rotational energy levels can be expressed in closed form as³

$$E_{J,K_{-1}} = \left(A - \frac{B+C}{2} \right) K_{-1}^2 + \left(\frac{B+C}{2} \right) J(J+1) \quad (1)$$

where A is the rotational constant $h^2/8\pi^2 I_a$, etc. The dipole moment of a rigorously prolate top is entirely along the symmetry or a axis with absorption selection rules (a type or parallel transition) $\Delta K_{-1} = 0$ and $\Delta J = 1$. If the molecule is only accidentally a near symmetric top, a dipole normal to the a axis is possible with selection rules (b type or perpendicular transition) $\Delta K_{-1} = 1$ and $\Delta J = 0, \pm 1$. These yield

$$\nu_a = (B+C)(J+1) \quad (2a)$$

$$\begin{aligned} \nu_b &= (2A - B - C)(K_{-1} + 1/2) & \Delta J &= 0 \\ &= (2A - B - C)(K_{-1} + 1/2) + \\ & \quad (B+C)(J+1) & \Delta J &= +1 \quad (2b) \\ &= (2A - B - C)(K_{-1} + 1/2) - (B+C)J & \Delta J &= -1 \end{aligned}$$

The b type $\Delta J = \pm 1$ transitions do not lead to superpositions and would be expected to be very weak and will not be considered further. The symmetric top spectrum is a series of equally spaced lines, each of which is a superposition of several transitions.

The effect of asymmetry is to split up the superimposed transitions. The asymmetry portion of the Hamiltonian is

$$H_{\text{asym}} = ((B-C)/2)(P_b^2 - P_c^2) \quad (3)$$

(3) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955.

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(1) E. B. Wilson, *Chem. Soc. Rev.*, 1, 293 (1972).
(2) (a) L. H. Scharpen and V. W. Laurie, *Anal. Chem.*, 44, 378R (1972); (b) S. Armstrong, *Appl. Spectrosc.*, 23, 575 (1969); (c) L. H. Scharpen, Paper O9, 24th Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, 1969; (d) V. Rautenstrauch and G. Ohloff, *Helv. Chim. Acta*, 54, 1776 (1971).

Table I. Comparison of High- and Low-Resolution Results

	κ	High-resolution constant ($B_0 + C_0$), MHz	Ref	Low-resolution constant ($B + C$), MHz	Ref
Benzaldehyde	-0.8216	2768.940	<i>a</i>	2785.3 ± 1	<i>d</i>
Iodobenzene	-0.965	1412.9 ± 0.2	<i>b</i>	1414.5 ± 0.2	<i>d</i>
<i>gauche</i> -Propyl [^{35}Cl]chloride	-0.8953	6175.64 ± 0.04	<i>c</i>	6160 ± 30	<i>e</i>
<i>trans</i> -Propyl [^{35}Cl]chloride	-0.98	4651.4 ± 0.4	<i>c</i>	4652.4 ± 1.4	<i>e</i>

^a Reference 13. ^b K. Johansson, H. Oldeberg, and H. Selen, *Ark. Fys.*, **29**, 531 (1965). ^c T. N. Sarachman, *J. Chem. Phys.*, **39**, 469 (1963).
^d This work. ^e Reference 2b.

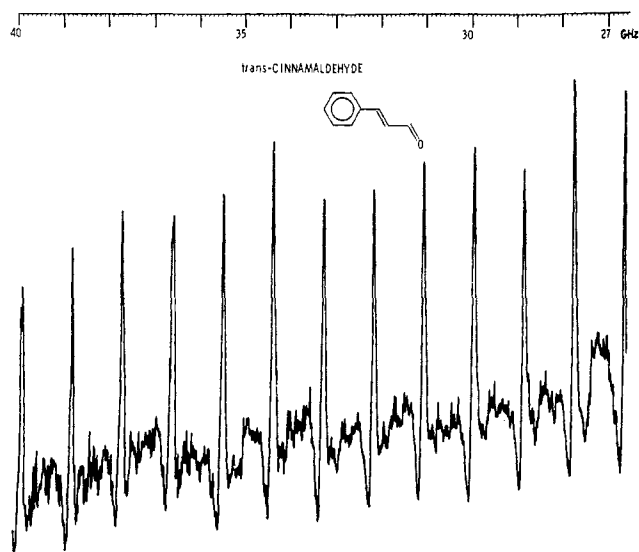


Figure 1. A typical low-resolution spectrum of a near-prolate symmetric top showing a simple series of equally spaced peaks.

which has nonvanishing matrix elements for $\Delta J = 0$ and $\Delta K_{-1} = \pm 2$. Only the $K_{-1} = \pm 1$ levels are affected by the perturbation H_{asym} to first order. The other levels are affected to second and higher order. To second order, the perturbation is inversely proportional to the energy spacing between the connected levels so that high K_{-1} levels may be only slightly affected by asymmetry while the lower K_{-1} levels may be strongly affected. Rotational transitions in the R band (26.5–40 GHz) of molecules such as cinnamaldehyde have J values of 20–40 and substantial numbers of high K_{-1} symmetric top-like transitions. If the asymmetry is large, the number of “symmetric top” transitions will be small, and the spectrum will be complex, diffuse, and weak. A useful measure of asymmetry is Ray’s parameter, $\kappa = (2B - A - C)/(A - C)$, which is -1 for a prolate top and $+1$ for an oblate top. We have found that molecules with κ in the range $-0.70 > \kappa > -1$ ($J = 20$ to 40) can exhibit well-defined band spectra.

Each band is much broader than an individual transition because of the spreading effect of the asymmetry, resulting in reduced resolution and accuracy in frequency measurement. In the cases we have observed, each band recorded under low-resolution conditions is sufficiently broad to encompass transitions in not only the ground but also excited vibrational states. With excited state data lacking, the calculation of a detailed line shape is impossible. In spite of this, the low-resolution rotational constant is a good approximation to the ground-state rotational constant obtained in high resolution (Table I), although the agree-

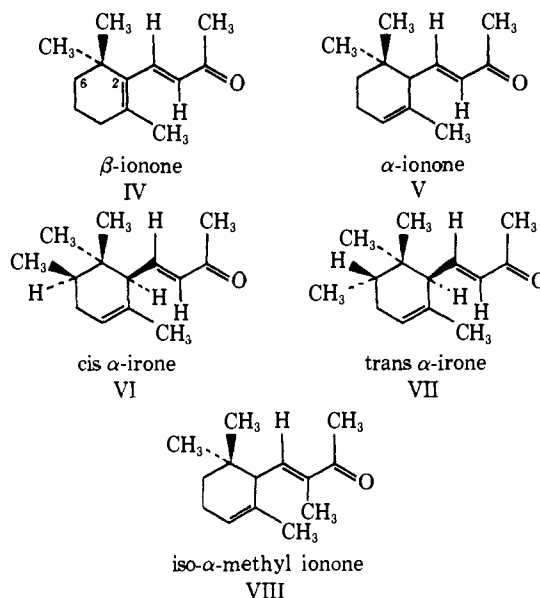


Figure 2. Structural formulas of ionones studied.

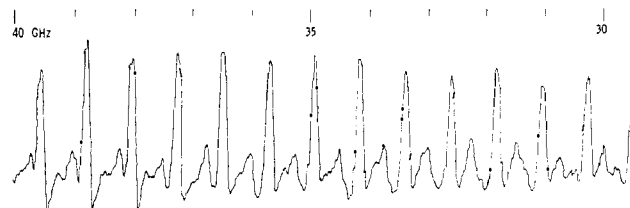


Figure 3. Low-resolution spectrum of pure α -ionone showing two conformers.

ment is worse with higher asymmetry. The bands of very nearly prolate molecules (e.g., *trans*-cinnamaldehyde) cannot be resolved into their components even under high-resolution conditions. With greater asymmetry (e.g., benzaldehyde), the individual components are resolvable. In these cases for purposes of LRMW, the structure is erased by recording under low-resolution conditions, rapid scan rates and large time constants.

Conformational Content of Spectra. In the absence of observable isotopic species, the number of different band series gives directly the number of near prolate conformers with a μ_a of ~ 0.5 D or larger (cf. Figure 3). Nmr is the only other spectroscopic technique that gives this type of information quickly and unambiguously, but it is not always possible to freeze out the interconversion of conformers with variable temperature studies. Comparison of calculated and observed rotational constants, $B + C$ and/or $2A - B - C$, gives the approximate conformation and stereochemis-

try of each species. Using bond angles and bond lengths obtained from spectroscopic and diffusion studies on smaller molecules, one can calculate rotational constants with a confidence of *ca.* 5% or better⁴ (Table II). Manipulation of the structural parameters

Table II. Comparison of Calculated and Observed Rotational Constants (MHz)

	$(B + C)_{\text{calcd}}$	$(B + C)_{\text{obsd}}$
<i>trans</i> -Cinnamaldehyde	1152	1106.3 ± 0.1
<i>p</i> -Anisonitrile	1380 (1346) ^a	1333.5 ± 0.1
<i>p</i> -Nitroanisole	1115 (1082)	1094.5 ± 0.1
<i>p</i> -Anisaldehyde		
<i>s</i> -Trans conformer	1368 (1330)	1311.2 ± 0.1
Nonplanar conformer(s)	1383 ^b (1341 ^b)	1323.5 ± 0.1
<i>s</i> -Cis conformer	1406 (1357)	1334.9 ± 0.1
α,α,α -Trideuterio- <i>p</i> -anisaldehyde		
<i>s</i> -Trans conformer	1293 (1251)	1235.0 ± 0.4
Nonplanar conformer(s)	1310 ^b (1263 ^b)	1248.1 ± 0.5
<i>s</i> -Cis conformer	1333 (1281)	1260.6 ± 0.9
<i>m</i> -Anisaldehyde (principal conformer)	1447 (1418)	1416 ± 1

^a Figures in parentheses are based on different structural assumptions (*vide infra*). ^b Methoxy group dihedral angle, φ , equals 90°.

to force exact agreement between theory and experiment is a dubious enterprise. Moderately sized molecules have several correlated parameters that strongly affect the rotational constants. LRMW alone is useful for conformational analysis not for accurate structure determination. If the molecule has several conformational degrees of freedom, assumptions or information from other techniques is necessary for a complete solution, since only one rotational constant is usually determined.

Although it is not possible to reproduce rotational constants exactly without excessive manipulation, the direction and semiquantitatively the magnitude of the change of rotational constants with conformational change can be accurately predicted. This permits the assignment of conformers of a single compound or closely related members of a homologous series. Comparison of data can sometimes result in conformational conclusions on all members of a series, particularly if one member is well characterized using other arguments. Isotope shifts can be used to locate atoms in a molecule,^{2a} although we have not explored this avenue yet.

A semiquantitative measure of the relative asymmetry of the species can be obtained from the line width which results from the spreading out of the transitions making up the band. With a Stark modulated spectrometer, the measurements should be made at high Stark voltages to minimize the interference of the Stark lobes. The line width is somewhat dependent on J since higher J bands will have more K_{-1} components that closely approach the symmetric top limit. The comparison of line width and amount of resolved structure is most valid within a series of closely related compounds. Even so, a reasonable correlation exists between κ calculated from assumed

structures and line width at half-height for molecules of widely varying rotational constants (Table III).

Table III. Dependence of Line Width on Asymmetry

	Line width, MHz	κ_{calcd}	$(B + C)_{\text{obsd}}$, MHz
<i>trans</i> -Cinnamaldehyde	64	-0.97	1106
Iodobenzene	65	-0.96	1114
<i>p</i> -Anisonitrile	68	-0.95	1334
<i>p</i> -Nitroanisole	68	-0.95	1094
<i>p</i> -Anisaldehyde (III)			
<i>s</i> -Trans conformer	62	-0.95	1311
<i>s</i> -Cis conformer	92	-0.93	1334
α -Ionone (V)	100	<i>ca.</i> -0.85	775
	120	<i>ca.</i> -0.85	749
β -Ionone (IV)	180	<i>ca.</i> -0.81	752

Although the line width of individual resolved transitions is pressure and power dependent, the line width of the composite band is independent of these effects. The effect of pressure in LRMW is to partially erase band structure. As a result, the intensity of a LRMW band is directly proportional to the partial pressure of the absorbing species. Relative intensities can be used to provide relative energy differences. However, aside from the usual difficulties in interpreting and obtaining relative intensity data,⁵ LRMW is beset with special difficulties. The bands are sufficiently broad that they are not completely modulated at the highest practical voltages. There is also the problem of overlap between adjacent bands and their Stark lobes. The extraction of relative populations from intensity data requires knowledge of the dipole moment components. Since the Stark effect is not resolved, this cannot be obtained by the usual techniques.³ The Lindfors and Cornwell rate of growth technique⁶ is not useful, since it requires a detailed line-shape analysis. Lacking direct experimental data, one can sometimes argue that the desired component does not significantly change with conformational alteration, or estimate the components using bond moments, or use the total dipole moments obtained from other techniques assuming that the unneeded components make a negligible contribution to the total. Finally, the dependence of bandwidth on asymmetry introduces another not easily treated factor that affects relative intensity. At best single temperature LRMW intensity data yield only order of magnitude thermodynamic data. These unknown, constant factors can be canceled by making measurements at different temperatures, yielding enthalpy changes, although this approach has not been tried yet.

Limitations of the Technique. A permanent electric dipole moment is a prerequisite for rotational transitions, and a large moment is desirable to obtain a good S/N ratio. For sensitivity reasons, Stark modulation is used in most spectrometers. The bands are sufficiently broad that a second-order Stark effect alone will not give a detectable signal. The symmetric top-like components of a band consist of closely spaced a dipole connected K_{-1} doublets so that the bands

(4) Computer programs written by R. Beaudet and H. Pickett are available, which convert bond lengths and bond angles into rotational constants.

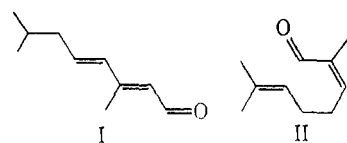
(5) A. S. Esbitt and E. B. Wilson, *Rev. Sci. Instrum.*, **34**, 901 (1963).

(6) K. L. Lindfors and C. D. Cornwell, *J. Chem. Phys.*, **42**, 149 (1965).

exhibit a first-order and sufficient Stark effect if $\mu_a \neq 0$. A μ_a of 0.5–1.0 D is probably necessary to provide enough modulation to detect either *a* or *b* type transitions. For example, the polar molecule anisole (small μ_a) does not have a LRMW spectrum whereas *p*-bromoanisole (large μ_a) does.

The molecule must be volatile, but a vapor pressure of *ca.* 30 μ is usually sufficient. This is a severe restriction, necessitating the preparation of derivatives in some cases. Resolution conditions also set an upper bound on the size of the molecule to be studied. If the rotational constants are too small (500 MHz), there will be severe overlapping of the bands.

If the molecule is too asymmetric ($|k| < 0.70$), there may be insufficient superposition to give a measurable spectrum. Citraldehyde does not exhibit a LRMW spectrum. This rules out the presence of a near prolate conformer I and indicates the preference for a more asymmetric form, such as II. Although this



restriction appears to be severe, a few bulky groups with quasi-axial symmetry such as *tert*-butyl or benzene or a heavy atom such as iodine or bromine, which is placed near the *a* axis, are often sufficient to give enough symmetry.

In LRMW only one rotational constant is usually determined, which may not be enough to sort out impurity bands from those of the compound of interest. This problem is especially serious if the potential impurities are closely related to the compound under study. Questions of purity are crucial. Trace impurities with narrow resolved lines would clearly stand out in the broad band spectrum if they were detected at all under the rapid scan conditions used in LRMW. In contrast to high-resolution spectra, the power absorbed is directly proportional to concentration. Since the most troublesome impurities will be closely related compounds with comparable line strengths, an impurity of 0.1% would not be detectable, a level achievable using chromatographic methods.

Applications

Cinnamaldehyde. Cinnamaldehyde ($C_6H_5CH=CH-CHO$) has a strong, relatively uncluttered *a* type spectrum (Figure 1). Two forms were observed with an approximate relative intensity of 0.042 ± 0.02 . If the μ_a and the line widths of the two conformers are assumed equal, this corresponds to an energy difference of 1.9 ± 0.3 kcal/mol. The bands of the less abundant conformer were for the most part overlapped with the main series. Accurate measurements were only possible on three weak bands. Because of overlap and weakness of the lines, it was not possible to measure the line width, but the presence of more structure indicated that the less abundant conformer was the more asymmetric.

In calculating rotational constants, the following bond lengths (ångströms) were used: CC (aromatic), 1.39; CH, 1.08; C=C, 1.36; CC, 1.46; C=O, 1.22. All bond angles were assumed to be 120° . Planarity

was also assumed as every heavy atom belongs to a conjugated π system, and nonplanarity would result in a loss of resonance energy. A large number of high-resolution microwave studies on conjugated polyenes have shown these systems to be planar,⁷ except in cases of severe steric repulsion where nmr studies have shown an equilibrium between planar and nonplanar forms.⁸ The closest nonbonded distance of approach (aldehyde and olefin protons) was calculated to be 2.44 Å which is slightly more than the sum of the van der Waals radii (2.40 Å⁹) so that steric repulsion is negligible in cinnamaldehyde.

The calculated rotational parameters for the four possible structures consistent with the above assumptions are compared with the experimental results in Table IV. The results quickly rule out the last two *cis*

Table IV. Cinnamaldehyde Rotational Constants

Structure	$(B + C)_{\text{calcd}}$, MHz	k_{calcd}
s-Trans trans (i)	1151.6	-0.966
s-Cis trans (ii)	1226.6	-0.958
s-Trans cis (iii)	1592.0	-0.848
s-Cis cis (iv)	2084.1	-0.702
Obsd	1106.3 ± 0.1^a	<i>Ca.</i> -0.96
	1179.1 ± 0.1	

^a Principal observed species.

structures. This fact is no surprise; the *trans* structure is in agreement with chemical intuition and had previously been established with chemical¹⁰ and nmr¹¹ evidence. The cinnamaldehyde used was chromatographically pure, and a mixture of *cis*-*trans* isomers would have been separable. Of the two observed species, the principal conformer has the smaller value of $B + C$. A comparison of calculated (-75.8 MHz) and observed (-72.8 MHz) differences in $B + C$ (*s*-*trans* minus *s*-*cis*) establishes that the principal conformer is *s*-*trans*.

Previous work on other conjugated polyenes has established that *s*-*trans* is usually preferred to *s*-*cis*,⁷

(7) (a) Methyl vinyl ketone: P. D. Foster, V. M. Rao, and R. F. Curl, *J. Chem. Phys.*, **43**, 1064 (1965); (b) acrolein: E. A. Cherniak and C. C. Costain, *ibid.*, **45**, 104 (1966); R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, *ibid.*, **26**, 636 (1957); (c) crotonaldehyde: S. L. Hsu and W. H. Flygare, *Chem. Phys. Lett.*, **4**, 317 (1969); M. Suzuki and K. Kozima, *Bull. Chem. Soc. Jap.*, **42**, 2183 (1969); (d) acryloyl fluoride: J. J. Kearns and R. F. Curl, *J. Chem. Phys.*, **48**, 3773 (1968); (e) acryloyl chloride: R. Kewkey, D. C. Hemphill, and R. F. Curl, *J. Mol. Spectrosc.*, **44**, 443 (1972); (f) acrylic acid and methyl acrylate: N. L. Owen, *J. Mol. Struct.*, **6**, 37 (1970); (g) 1-cyanobutadiene: W. B. Dixon, Paper C8, 18th Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, 1963; (h) 1-methylbutadiene: S. L. Hsu and W. H. Flygare, *J. Chem. Phys.*, **52**, 1053 (1970); (i) 1,1-difluorobutadiene: R. A. Beudet, *J. Amer. Chem. Soc.*, **87**, 1390 (1965); (j) 1,1-difluoro-3-methylbutadiene: Y. S. Huang and R. A. Beudet, *J. Mol. Spectrosc.*, **34**, 1 (1970); (k) isoprene: D. R. Lide, *J. Chem. Phys.*, **37**, 2074 (1962).

(8) 1,1,3-Trihalobutadienes: A. A. Bothner-By and D. Jung, *J. Amer. Chem. Soc.*, **90**, 2342 (1968); and A. A. Bothner-By and D. F. Koster, *ibid.*, **90**, 2351 (1968).

(9) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1967, p 452.

(10) G. Gamboni, V. Theus, and H. Schinz, *Helv. Chim. Acta*, **38**, 255 (1955).

(11) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

but this is the first spectroscopic verification for cinnamaldehyde. Ultrasonic relaxation measurements have been interpreted in terms of an *s-trans*, *s-cis* equilibrium,¹² giving $\Delta H = 1.5$ kcal/mol, which agrees with the approximate LRMW result. The activation parameters for conversion from *s-trans* to *s-cis* were determined in the same study to be $\Delta H = 5.62$ kcal/mol and $\Delta S = -3.05$ eu. The order of calculated asymmetry parameters is also in agreement with the assignment, *s-trans* being more symmetric than *s-cis*.

***p*-Anisaldehyde (III).** III (Figure 4) has two conformational degrees of freedom, rotation of the aldehyde group and of the methoxy group. This gives rise to four possible conformers, two planar and two nonplanar. In interpreting the band spectrum, the following bond lengths (ångströms) were used in the calculation of rotational constants and interatomic distances: CH (aromatic), 1.08; CC (aromatic), 1.39; C=O, 1.22; C(ring)O, 1.35; C(top)O, 1.416; C(top)-H, 1.09. The COC angle in the methoxy top was assumed to be 111.5°, the COH angle in phenol;¹⁷ the HCO angle in the top, 109.5°; and all other angles, 120°. The rotational constants were also calculated (figures in parentheses, Tables II and V) for a COC angle of 120° and a 4° tilt of the C(ring)O bond, the electron diffraction results for anisole.¹³ The calculations (Table II) predict that $B + C$ for the rotomers falls in the order *s-trans* < nonplanar < *s-cis* (opposite order for $2A - B - C$).

The nonplanar rotational constants are close to the average of the planar constants. Furthermore, the rotational constants for the two nonplanar forms are practically identical (within a few megacycles per second of each other), so the LRMW spectra of these hypothetical forms would not be resolved into two distinct band series.

The moderately strong spectrum of normal and α,α,α -trideuterio isotopic species of III is a superposition of three sets of *a* type band spectra of comparable intensity, confirming that both the planar forms and at least one of the nonplanar forms are present. Comparison of the calculated and observed rotational constants supports this conclusion. The spectrum of the normal isotopic species also displays four weaker barely resolved *b* type bands falling into two series. On the basis of the rotational constants ($2A - B - C$), the two series were assigned to the *s-trans* form (obsd 7709 ± 10 MHz, calcd¹⁴ 8086 MHz) and the nonplanar form(s) (obsd 7607 ± 10 MHz, calcd 7398 MHz). Presumably, the two *b* type bands of the *s-cis* form in the range of the spectrometer (26.5–40 GHz) were overlapped by bands of the stronger *a* type spectrum. Although the LRMW data are ambiguous as to the identify of the nonplanar rotomer, a likely candidate is the form with an out-of-plane methoxy group. Steric hindrance, which favors nonplanarity, is large at the methoxy end of the molecule where the distances between the top and ring protons (1.2–1.9 Å) are significantly less than the sum of the van der Waals radii (2.4 Å).

Results of the other anisole derivatives indicate that

(12) M. S. DeGroot and J. Lamb, *Proc. Roy. Soc., Ser. A*, 242, 36 (1957).

(13) H. Seip, University of Oslo, private communication.

(14) The calculated values of $2A - B - C$ for III are based on the structure with the 4° tilt.

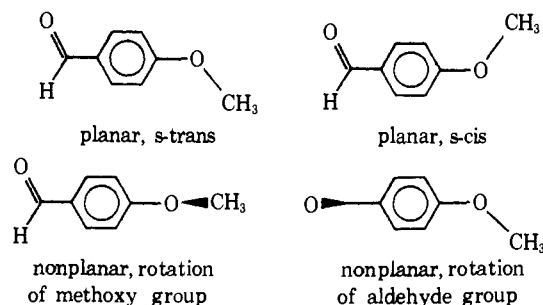


Figure 4. Possible conformers of *p*-anisaldehyde (III).

III may be unique in exhibiting a mixture of planar and nonplanar conformers. A nonanisole system that does exhibit this feature is the highly substituted 1,1,3-trihalobuta-1,3-dienes.⁸ The electron diffraction of anisole at 55° is consistent with a planar structure, and the 255° data indicate a low barrier.¹³ A microwave study of *p*-fluoroanisole also gives a planar structure with no evidence of tunneling (barrier greater than *ca.* 1.7 kcal/mol).¹⁵ The LRMW spectrum of *m*-anisaldehyde, which is broad, weak, and cluttered, shows three conformers (Table V). Four

Table V. *m*-Anisaldehyde Conformers^a

	$(B + C)_{\text{calcd}}$, MHz	κ_{calcd}	$(B + C)_{\text{obsd}}$, MHz
A	1229 (1919)	-0.22	Not observed
B	1587 (1551)	-0.79	1570 ± 2
C	1649 (1663)	-0.71	1623 ± 4
D	1447 (1418)	-0.91	1416 ± 1

^a Approximate relative intensities: $B:C:D = 9:9:22$.

planar conformers are possible, but one is too asymmetric ($\kappa = -0.22$) to exhibit a band spectrum. The three series are assignable to the near-prolate planar forms without invoking nonplanarity.

Ionone. β -Ionone (IV), a violet essence,¹⁶ was examined as a model for the study of the cyclohexenyl ring orientation in the visual chromophore retinal.¹⁷ As an aid to the conformational analysis of IV, the related perfume components (Figure 2), α -ionone (V), *cis*- α -ionone (VI), *trans*- α -ionone (VII), and iso- α -methylionone (VIII), were also studied. The LRMW results are given in Table VI. In these five compounds, there are numerous possibilities for isomerism, as tabulated in Table VII. These will be taken up one by one, together with the evidence for the preferred geometry. It will become clear that the interpretation of the LRMW data depends on results from nmr studies and structural assumptions based on studies of similar molecules.

(15) D. G. Lister and N. L. Owen, *J. Chem. Soc., Faraday Trans. 2*, 69, 1304 (1973).

(16) G. Uhde and G. Ohloff, *Helv. Chim. Acta*, 55, 2621 (1972).

(17) G. Wald, *Science*, 162, 230 (1960).

Table VI. Ionone Structural Parameters

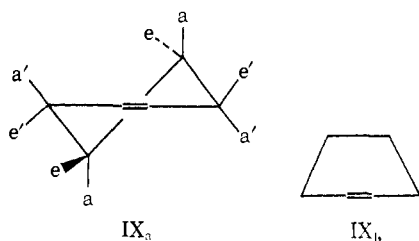
	(B + C) _{obsd} , MHz	Line width, MHz
β-Ionone (IV)	752.5 ± 0.2	180
α-Ionone (V)	775.1 ± 0.1 ^a	100
	749.2 ± 0.1	120
cis-α-Ironone (VI)	642.0 ± 0.1	80-100
trans-α-Ironone (VII)	687.0 ± 0.2 ^a	80-100
	694.6 ± 1.0	?
Iso-α-methylionone (VIII)	726.8 ± 0.1 ^a	52
	702.9 ± 0.1	50

^a More stable conformer.

Table VII. Isomerism in Ionones and Irones

Possible geometries	Assumed or found geometry
Ring	
Half-chair vs. half-boat	Half-chair
6-CH ₃ (VI and VII only), cis or trans to side chain	Both species investigated
Side chain position, pseudoaxial or pseudoequatorial	IV, inapplicable VI, pseudoequatorial only V, VII, VIII, both forms
Side chain: $\begin{array}{c} \diagup \text{CH}=\text{CH} \diagdown \\ \phi \qquad \qquad \qquad \chi \\ \diagdown \text{COCH}_3 \end{array}$	
First C-C, angle ϕ	-60 to +60°
C=C, cis or trans	Trans
Second C-C, angle χ	s-Trans

Ring Conformation. A cyclohexene ring can minimize the internal rotation energies about the five C-C bonds in two conformations, the so-called half-chair (IX_a) and half-boat (IX_b) forms. For each ionone,



rotational constants and the change of rotational constants with each conformational degree of freedom were calculated. The range of calculated rotational constants for the half-chair and half-boat forms overlapped, so that the ring conformation cannot be determined by LRMW. However, high-resolution microwave studies of cyclohexene¹⁸ itself and cyclohexene oxide,¹⁹ as well as an electron diffraction study of 1-methoxycyclohexene,²⁰ all show only the half-chair form. X-Ray crystallographic studies yield the same half-chair form for 2,3,4,5,6-pentachlorocyclohex-1-ene,²¹ the B ring (cyclohexenyl portion) of cholesteryl iodide,²² and the ionone-related retinal derivatives, *all-trans*-²³ and 9-*cis*-²⁴-β-ionylidene crotonic acid, mono-

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clinic²⁵ and triclinic²⁶ *all-trans*-retinoic acid, *all-trans*-15,15'-dehydro-β-carotene,²⁷ β-carotene,²⁸ 15,15'-dehydrocanthaxanthin,²⁹ and canthaxanthin.³⁰ Finally, theoretical studies confirm the greater stability of the half-chair form with an estimated energy difference between the forms of 2.7 kcal/mol.³¹ With this energy difference and the assumption of comparable dipole moment components, the half-boat form would have a spectrum only one-hundredth as intense as the half-chair form and would probably be undetectable. For the above reasons, only the half-chair form was considered for all five compounds.

Side Chain, C=C. The stereochemistry about the C=C bond in the side chain can be either *cis* or *trans*. Tribolet and Schinz showed by chemical means that V is *trans*.³² Ohloff recently established by nmr that V, VI, and VII are *trans*.^{24,33} As a check, the nmr of all the ionone samples handled was investigated, confirming that the C=C side chain stereochemistry is *trans*.

Side Chain, Angle χ . Rotational isomerism is conceivable about the C-C between the two double bonds in the side chain (C_γ-C_δ). The five compounds can be thought of as *trans*-substituted methyl vinyl ketones. The substituent (one of the various cyclohexenes) is far enough removed in space from the above C-C bond that one would expect it to have little effect on the conformation at C_γC_δ. Methyl vinyl ketone has been found to be planar and *s-trans*,^{7a} with no evidence for the other forms so the planar *s-trans* form is presumably at least the dominant form. The same configuration is assumed here for all five compounds. The fact that IV and VI show only one conformer in their LRMW spectra supports the conclusion that the side chain exists in only one form for all five compounds.

Side Chain Position. The half-chair cyclohexene ring (IX_a) has four types of substituents: true axial (a), true equatorial (e), pseudoaxial (a'), and pseudoequatorial (e'). In the discussion to follow, the ionone conformer with the side chain in the pseudoequatorial position will be referred to as the pseudoequatorial conformer with a similar definition of the pseudoaxial conformer. For species V, VII, and VIII, two isomers are indicated by the LRMW spectra but only one form for IV and VI. A reasonable explanation of these facts is that in V, VII, and VIII the side chain could be attached to the pseudoequatorial or pseudoaxial positions, giving rise to two sets of bands. However, in IV there is only one position for the side chain (it is on a double bonded carbon), and in VI models show that a strong steric repulsion between the 6-methyl group and the side chain would destabilize the pseudoaxial conformer. The LRMW results (*vide infra*) are in agreement with the conformer being pseudoequatorial.

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Side Chain, Angle ϕ . The angle ϕ about the C-C ($C_\beta-C_{\beta'}$) attaching the side chain to the ring is more troublesome than the angle χ . The X-ray structures of triclinic *all-trans*-retinoic acid,²⁶ 9-*cis*- β -ionylidene crotonic acid,²⁴ and *all-trans*-15,15'-dehydro- β -carotene²⁷ show distorted s-*cis* conformations with ϕ in the range 35–80°. However, the crystal structures of monoclinic *all-trans*-retinoic acid²⁵ and *trans*- β -ionylidene crotonic acid²³ show a distorted s-*trans* conformation. Furthermore, the diffuse spectrum of *all-trans*-retinal in a rigid glass at 77°K is consistent with statistical broadening resulting from conformational disorder of the ring orientation.³⁴ Karplus, *et al.*,³⁵ have studied the ring orientation in IV, *all-trans*-retinal, and 11-*cis*-retinal by means of semiempirical calculations and also by interpretation of nmr measurements of the nuclear Overhauser effect and long range coupling constants. The calculations suggest that strong steric repulsions destabilize the usually preferred s-*trans* configuration. A broad, flat minimum in the range $\phi = 40$ –120° is predicted. The nmr results yield a distorted s-*cis* configuration with the torsional angle ϕ in the range 30–70°.

The LRMW spectra can be brought to bear on the problem of estimating ϕ . With the assumption of the half-chair ring form, the *trans* olefinic side chain, the planar s-*trans* CC=O conformation, and the bond lengths and bond angles used by Karplus, *et al.*, in their calculations,³⁶ the calculated values of $B + C$ and the asymmetry parameter κ are plotted against the dihedral angle (ϕ is zero when $C_\beta H_\alpha$ and $C_{\beta'} H_{\alpha'}$ are coplanar and in the same direction) for β -ionone (IV) and the two forms, pseudoaxial (V_a) and pseudo-equatorial (V_b), of α -ionone (Figure 5). The confidence limits on the calculated parameters are estimated to be $\pm 5\%$. For simplicity of display, the experimental values rather than the calculated curves are bracketed with these confidence limits in Figure 5. The experimental values of $B + C$ and the line widths agree best for ϕ from -60 to 60° . This range overlaps the range obtained by Karplus, *et al.*, discussed above. Within this range of ϕ , the two conformers of V, VII, and VIII have comparable asymmetries by calculation and as observed from the bandwidths. Since the calculated $B + C$ are lower for the pseudo-equatorial than for the pseudoaxial form of V, the conformer with the observed smaller value of $B + C$ (which is the one with less intensity and thus probably less abundance) is most likely the pseudo-equatorial form. For VII and VIII, the calculated curves for the forms are particularly close together so that the assignment is uncertain.

6-Methyl Stereochemistry. In the case of the irones (VI and VII), *cis*-*trans* isomerism is possible across the ring, since the lone 6-methyl group on the ring can be either *cis* or *trans* to the side chain. Both forms are known and were assigned by Ohloff and Rautenstrauch in a chemical determination of their absolute configuration.^{2d,33} They established that the first eluted

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(36) 120° trigonal angles, 109° 28' tetrahedral angles, 1.46 Å conjugated single bonds, 1.35 Å conjugated double bonds, 1.34 Å unconjugated double bonds, 1.52 Å sp²sp³ single bonds, 1.54 Å sp³sp³ single bonds, 1.082 Å CH bonds, and 1.22 Å C=O bond.

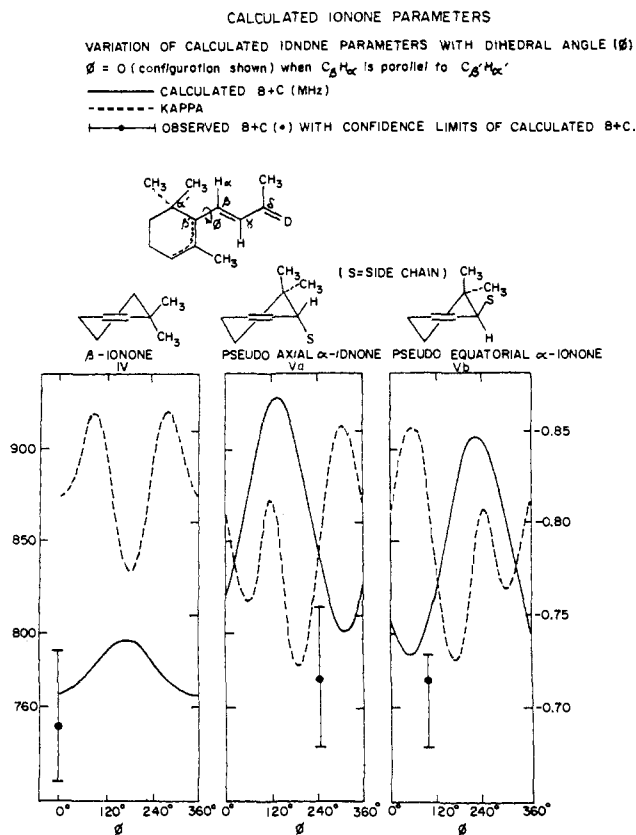


Figure 5. Calculated ionone parameters.

isomer in the vpc separation (Carbowax 20M column) was *trans* (VIII). Using the same column, we found that the LRMW spectrum of the first eluted isomer showed two species with a $B + C$ of 687 and 695 MHz and the second eluted isomer, a single species, with a $B + C$ of 642 MHz. The minimum calculated $B + C$ (ϕ in the range -60 to 60°) for the *cis* pseudo-equatorial, *cis* pseudoaxial, *trans* pseudo-equatorial, and *trans* pseudoaxial species are 680, 880, 720, and 725 MHz, respectively. Since our confidence in calculating $B + C$ is *ca.* $\pm 5\%$, the second eluted (642 MHz) isomer is *cis* with a preference of the pseudo-equatorial conformation. The first eluted isomer, by elimination, is *trans*, and as discussed above, the two species observed correspond to the pseudoaxial and pseudo-equatorial conformers. This assignment of the *cis*-*trans* ring stereochemistry is in agreement with the work of Ohloff and Rautenstrauch. This result, which required much less effort than the chemical route, illustrates the power of LRMW.

It is unlikely that molecules with more conformational complexity than the ionones can be tackled by LRMW with complete success. Even here, a complete analysis of β -ionone (IV) was not possible. The calculated parameters, $B + C$ and κ , are relatively insensitive to ϕ so that the experimental data are consistent with a very wide range of ϕ . At best, one can conclude that the results are consistent with the more precise work of Karplus, *et al.* Fortunately, the other ionones studied are more sensitive to ϕ so that this quantity was better determined for V–VIII.

Experimental Section

All microwave measurements were made on a Hewlett-Packard

Model 8460A MRR R band spectrophotometer. Scan rates of 10 and 1 MHz/sec with time constants of 0.3–1 sec were usually used. Longer time constants were avoided because of spectral distortion at these sweep rates. Frequency measurements were based on the average of the position of peak maximum in forward and reverse scans. Frequency accuracy depended on the width of the bands and varied from 1 to 20 MHz. To maximize the signal, a sample pressure of 100 μ (if possible) and a Stark voltage of 1800 V were used. Higher pressures were avoided because of danger of arcing in the cell. All liquid samples were injected using the direct inlet port to minimize the effect of volatile trace impurities.

Room temperature nmr measurements were made on a Varian A-60 nmr spectrometer using CCl_4 as a solvent and cyclohexane as internal reference. With the exception of isotopic modifications and methyl ionones, all compounds were obtained from the usual commercial sources. A 50–50 mol % mixture of VI and VII (Irene Alpha) and VIII were obtained from Givaudan Corp. α, α, α -Trideuterio-*p*-anisaldehyde was prepared in a Williamson synthesis³⁷

by a reaction in heavy water of the sodium salt of *p*-hydroxybenzaldehyde with perdeuteriodimethyl sulfate (Aldrich). All materials were purified, if necessary, and assayed using vapor phase chromatography (vpc) on a Carbowax 20M column at 160°. Isotopic and isomeric purity and identity were checked using nmr. In cases where in spectrometer isomerization was feared, the material was injected into the spectrometer, recovered, and analyzed by vpc.

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Medium Effects and Quantum Yields in the Photoaddition of Naphthalene and Acrylonitrile.¹ Chemical Evidence on an Exciplex Structure

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Abstract: The photoaddition of naphthalene and acrylonitrile at 313 nm and in hydroxylic solvents to afford *endo*-7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-diene (1), the *endo*-8-isomer, and 1- and 2-naphthylpropionitrile (3 and 4) is investigated. The reactive state is naphthalene S_1 which is determined by kinetically relating quantum yields and fluorescence quenching dependences on acrylonitrile concentration. The fluorescence quenching is proposed to occur by charge-transfer exciplex formation. Good Stern–Volmer plots are obtained for quenching in acetonitrile and *tert*-butyl alcohol, and the rate constant for the latter is $14 \times 10^7 M^{-1} \text{sec}^{-1}$. Fluorescence of indene and anthracene is also quenched, the rate for indene being diffusion controlled. The dilution plot of reciprocal quantum yield against reciprocal acrylonitrile concentration is linear if 2,3-dimethylbuta-1,3-diene is added to prevent triplet-sensitized decomposition of 1. It is proposed that the exciplex responsible for fluorescence quenching has a polar structure, and the substituted products 3 and 4 arise from protonation of the exciplex. The evidence is that (i) the fraction of substitution increases with medium polarity and (ii) reaction in deuterioxyated solvents gives 3 and 4 labeled in the methyl groups. It is believed that indene reacts similarly and some results for the latter are presented. The exciplex structure is discussed. A correlation exists between the energetics of electron transfer and exciplex behavior for some reactions of naphthalene and benzene derivatives and acrylonitrile. This correlation may be of useful predictive value.

Formation of excimers³ or exciplexes⁴ by reaction with ground-state molecules is an important mode of deactivation of numerous excited states. The rapid chemical reactions which give rise to exciplexes have been extensively studied, mainly by fluorescence quenching measurements, and a number of reviews have been published.^{3,5–8}

There is convincing evidence that charge- and electron-transfer processes are important in the formation and decay of many exciplex species. For example, rates of quenching are known to depend on the donor–acceptor properties of the quenchee and quencher,⁹ and good correlations of quenching rates with ionization potentials,^{10–15} and with oxidation and reduction

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